Methods for Analyzing Resonances in Atomic Scattering

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Abstract

Resonances, which are also described as autoionizing or quasi-bound states, play an important role in the scattering of atoms and ions with electrons. The current article is an overview of the main methods, including a recently-proposed one, that are used to find and analyze resonances.

Keywords: atomic scattering; resonance; autoionizing states; quasi-bound states; **R**-matrix; **K**-matrix method; **QB** method; time-delay method.

1 Introduction

In atomic scattering, resonance occurs when a colliding continuum electron is captured by an ion to form a doubly excited state. The resonant state is normally short lived and hence it is permanently stabilized *either* by a radiative decay of the captured electron or an electron in the parent to a true bound state of the excited core ion *or* by autoionization to the continuum with the ejection of an electron. In most cases the stabilization occurs through the second route, i.e. by autoionization rather than radiative decay. These excited autoionizing systems have a distinctive signature on the photoionization cross sections.

The resonance phenomenon is a highly important feature in atomic collisions as it plays a vital role in the ionization balance of thermodynamic systems and their radiative emissions. The Auger effect is one of the early examples of the resonance effects that have been discovered and extensively investigated [1, 2]. The reader is advised to consult other references in the literature of atomic physics (e.g. [1, 3]) for a general historical background.

The shape of resonance scattering cross section as a function of photon energy is determined by the background shift. Several symmetric and asymmetric line shapes have been proposed to model resonance profiles for different situations; these profiles include Lorentz, Shore and Fano, as given in Table 1. Resonance characteristics; such as their position on the energy axis, area under profile and full width at half maximum; are usually obtained by fitting the profile of the autoionizing state to a fitting model such as Lorentz. These characteristics have physical significance; for example the width of a resonance quantifies the strength of the interaction with the continuum and hence autoionization probability and lifetime, while the contribution of a resonance to the recombination rate correlates to the area underneath and hence it quantifies the probability of radiative decay [3–7].

Table 1: The commonly-used resonance line profiles where σ is the photoionization cross section, A is a proportionality factor with the dimension of area, Δ_E is the full width at half maximum, E is the energy, E_r is the resonance position on the energy line, $p = \frac{2(E-E_r)}{\Delta_E}$, α and β are parameters related to the dipole and Coulomb matrix elements, and k is the Fano asymmetry factor.

Profile	Equation
Lorentz	$\sigma = A \frac{\Delta_E^2/4}{(E-E_r)^2 + \Delta_E^2/4}$
Shore	$\sigma = A \frac{\alpha p + \beta}{p^2 + 1}$
Fano	$\sigma = A \frac{(k+p)^2}{p^2 + 1}$

2   Methods for Investigating Resonances

There are several methods for finding and analyzing resonances. In the following sections we outline three of these methods which are all based on the use of the reactance **K**-matrix of the **R**-matrix theory for atomic and molecular scattering calculations. The advantage of this common approach, which employs the close coupling approximation, is that resonance effects are naturally delineated, since the interaction between bound and free states is incorporated in the scattering treatment.

2.1   QB Method

A common approach for finding and analyzing resonances is to apply a fitting procedure to the reactance matrix, **K**, or its eigenphase as a function of energy in the neighborhood of an autoionizing state. However, fitting the **K**-matrix itself is complicated because the reactance matrix has a pole at the energy position of the autoionizing state. An easier alternative is to fit the arc-tangent of the reactance matrix. The latter approach was employed by Bartschat and Burke [2] in their fitting code RESFIT.

The eigenphase sum is defined by

$$\delta = \sum_{i=1}^{N} \arctan \Lambda_i \qquad (1)$$

where Λ_i is an eigenvalue of the **K**-matrix and the sum runs over all open channels interacting with the autoionizing state. The eigenphase sum is normally fitted to a Breit-Wigner form

$$\delta = \bar{\delta} + \arctan\left(\frac{\Delta_r}{2\left(E_r - E\right)}\right) \qquad (2)$$

where $\bar{\delta}$ is the sum of the background eigenphase, Δ_r is the resonance width, E_r is the energy position of the resonance, and E is the energy. This approach was used by Tennyson and Noble [8] in their fitting code RESON [9].

In theory, an autoionizing state exhibits itself as a sharp increase by π radians in the eigenphase sum as a function of energy superimposed on a slowly-varying background. However, due to the finite width of resonances and the background variation over their profile, the increase may not be by π precisely in the actual calculations. A more practical approach then is to identify the position of the resonance from the energy location where the increase in the eigenphase sum is at its highest rate by having a maximum gradient with respect to the scattering energy, i.e. $(d\delta/dE)_{max}$ [8, 10, 11].

The **QB** method of Quigley and Berrington [10] is a computational technique for finding and analyzing autoionizing states that arise in atomic and molecular scattering processes using eigenphase fitting. The essence of this method is to apply a fitting procedure to the reactance matrix eigenphase near the resonance position using the analytic properties of the **R**-matrix theory. The merit of the **QB** method over other eigenphase fitting procedures is that it utilizes the analytical properties of the **R**-matrix method to determine the variation of the reactance matrix with respect to the scattering energy analytically. This analytical approach

can avoid possible weaknesses, linked to the calculations of **K**-matrix poles and arc-tangents, when numerical procedures are employed instead. The derivative of the reactance matrix with respect to the scattering energy in the neighborhood of a resonance can then be used in the fitting procedure to identify the energy position and width of the resonance.

The **QB** method begins by defining two matrices, **Q** and **B**, in terms of asymptotic solutions, the **R**-matrix and energy derivatives, such that

$$\frac{d\mathbf{K}}{dE} = \mathbf{B}^{-1}\mathbf{Q} \tag{3}$$

The eigenphase gradients of the **K**-matrix with respect to energy can then be calculated. This is followed by identifying the resonance position, E_r, from the point of maximum gradient at the energy mesh, and the resonance width, Δ_r, which is linked to the eigenphase gradient at the resonance position, $\delta'(E_r)$, by the relation

$$\Delta_r = \frac{2}{\delta'(E_r)} \tag{4}$$

This equation may be used to calculate the widths of a number of resonances in a first approximation. A background correction due to overlapping profiles can then be introduced on these widths individually to obtain a better estimate.

The **QB** method was implemented in the STGQB code of Quigley and coworkers [12] as an extension to the **R**-matrix code. It should be remarked that Busby *et al* [11] have used a similar method for finding and analyzing resonances graphically by their VisRes program.

2.2 Time-Delay Method

The Time-Delay method of Stibbe and Tennyson [13] is based on the time-delay theory of Smith [14] where use is made of the lifetime eigenvalues to locate the

resonance position and identify its width. According to this theory, the time-delay matrix $\mathbf{M}$ is defined in terms of the scattering matrix $\mathbf{S}$ by

$$\mathbf{M} = -\mathrm{i}\,\hbar\,\mathbf{S}^* \frac{d\mathbf{S}}{dE} \tag{5}$$

where i is the imaginary unit, $\hbar\ (= h/2\pi)$ is the reduced Planck's constant, $\mathbf{S}^*$ is the complex conjugate of $\mathbf{S}$, and E is the energy. It has been demonstrated by Smith [14] that the eigenvalues of the $\mathbf{M}$-matrix represent the collision lifetimes and the largest of these eigenvalues corresponds to the longest time-delay of the scattered particle. For a resonance, the time-delay has a Lorentzian profile with a maximum precisely at the resonance position. By computing the energy-dependent time-delay from the reactance matrix, and fitting it to a Lorentzian peak shape, the resonance position can be located and its width is identified.

This method, as implemented in the TIMEDEL program of Stibbe and Tennyson [13], uses the reactance $\mathbf{K}$-matrix as an input, either from a readily-available archived scattering calculations or from dynamically-performed computations on an adjustable mesh. The $\mathbf{S}$-matrix is then formed using the relation

$$\mathbf{S} = \frac{\mathbf{I} + \mathrm{i}\mathbf{K}}{\mathbf{I} - \mathrm{i}\mathbf{K}} \tag{6}$$

where $\mathbf{I}$ is the identity matrix, and i is the imaginary unit. The time-delay $\mathbf{M}$-matrix is then calculated from Equation 5, with numerical evaluation of the $\mathbf{S}$-matrix derivative, and diagonalized to find the eigenvalues and hence obtain the longest time-delay of the incident particle. Approximate resonance positions are then identified from the energy locations of the maxima in the time-delay profile, and the widths are estimated from the Lorentzian fit. On testing the degree of overlapping of neighboring resonances, TIMEDEL decides if the resonances should be fitted jointly or separately.

2.3   K-Matrix Method

This is a novel method proposed by P.J. Storey [private communication] and elaborated and implemented in the free stage (STGF) of the **R**-matrix code by Sochi [7]. The essence of this method is to identify the resonance position and width from locating the poles of the **K**-matrix on the energy mesh. The method is based on the fact that resonances arise from poles in the scattering matrix **S** which varies slowly with energy. The **K**-matrix method exploits the fact that for the low-lying resonances just above the ionization threshold, the scattering matrix **S** has only one channel, and hence the reactance matrix, **K**, is a real scalar with a pole near the resonance position at the energy mesh.

According to the collision theory of Smith [14], the lifetime matrix **M** is related to the **S**-matrix by Equation 5. Now, a **K**-matrix with a pole at energy E_0 superimposed on a background K_o can be approximated by

$$K_i = K_o + \frac{\text{g}}{E_i - E_0} \tag{7}$$

where K_i is the value of the **K**-matrix at energy E_i and g is a physical parameter with dimension of energy. In Appendix A it is demonstrated that in the case of single-channel scattering the **M**-matrix is real with a value given by

$$M = \frac{-2\text{g}}{(1 + K_o^2)(E - E_0)^2 + 2K_o\text{g}(\text{E} - \text{E}_0) + \text{g}^2} \tag{8}$$

Using the fact demonstrated by Smith [14] that the lifetime of the state is the expectation value of M, it can be shown from Equation 8 that the position of the resonance peak E_r is given by

$$E_r = E_0 - \frac{K_o\text{g}}{1 + K_o^2} \tag{9}$$

while the full width at half maximum Δ_E is given by

$$\Delta_E = \frac{|2g|}{1 + K_o^2} \tag{10}$$

The two parameters of primary interest are the resonance energy position E_r, and the resonance width Δ_r which equals the full width at half maximum Δ_E. However, for an energy point E_i with a **K**-matrix value K_i, Equation 7 has three unknowns, K_o, g and E_0, which are needed to find E_r and Δ_r. Hence, three energy points at the immediate neighborhood of E_0 are required to identify these unknowns. As the **K**-matrix changes sign at the pole, the neighborhood of E_0 is located by testing the **K**-matrix value at each point of the energy mesh for sign change. Consequently, the three points are obtained and used to find E_r and Δ_r. Complete derivation of the **K**-matrix method is given in Appendix A.

With regard to sampling the three points for the **K**-matrix calculations, it was observed in our implementation that sampling the points very close to the pole makes the energy position and width of resonances susceptible to fluctuations and instabilities. Therefore, a sampling scheme in which the points are selected from a broad range not too close to the pole should be employed. This approach can be implemented by generating two meshes, coarse and fine, around the pole as soon as the pole is found. The reliability of the sampling scheme can be tested by using several different three-point combinations for each resonance where all these combinations should produce virtually identical results for the position and width of the resonance.

To improve the performance of the **K**-matrix method an interactive graphical technique may be used to read the **K**-matrix data directly and plot it against energy or arbitrary ordinal number while searching for poles. With a reasonably fine mesh, a positive or negative pulse in the graph appears even when the background is sufficiently large to prevent sign-change. As soon as this is detected, the search

is stopped and resumed at higher resolution by focusing on a very narrow energy band using a fine mesh, and hence very small number of energy points are needed to find the resonance. The strategy is to start the search with a coarse mesh over the suspected energy range. If the glitch failed to appear, the search is repeated with finer mesh until the glitch is observed. This graphical technique is essential for finding resonances in reasonably short time.

A non-graphical tools for pole search may also be used for the purpose of searching for any sudden increase or decrease in the background of the **K**-matrix. As soon as this is detected, a search for poles with a finer mesh can be resumed. These non-graphic tools can be more efficient than the graphic tools, and hence they can help substantially in finding most of the resonances with limited time and computational effort.

A comparative investigation between the **K**-matrix and **QB** on the C II resonances [7] demonstrated that these methods produce virtually identical results. However, the **K**-matrix is computationally superior in terms of the required computational resources, mainly CPU time, especially when coupled with the above-mentioned interactive graphic and non-graphic techniques by first applying a coarse energy mesh and then zooming with a fine mesh over a very limited energy band as soon as a sign of resonance appears, i.e. a glitch in the smoothly-varying background is detected. Nevertheless, the **QB** method is more general as it deals with multi-channel resonances, as well as single-channel resonances, while the **K**-matrix method in its current formulation is restricted to single-channel resonances. Although in principle the **K**-matrix method can be extended to multi-channel resonances, it is expected to lose its main advantage which originates from the scalar nature of the scattering, reactance, and time delay matrices in the case of single-channel resonances since for multi-channel cases these matrices will not be scalars any more.

3 Conclusions

The resonance phenomenon plays very important role in the atomic scattering processes and subsequent transitions. Several methods based on different theoretical backgrounds are proposed and used to find resonances and identify their parameters. In this article, we outlined three methods for finding and analyzing resonances, including the recently developed $\mathbf{K}$-matrix method, which is highly efficient for investigating single-channel resonances near the ionization threshold.

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4   Nomenclature

α parameter in Shore profile

β parameter in Shore profile

Γ^a autoionization transition probability (s^{-1})

δ eigenphase sum

$\overline{\delta}$ eigenphase background

δ' eigenphase gradient of **K**-matrix with respect to energy (J^{-1})

Δ_E full width at half maximum of resonance as function of energy (J)

Δ_r width of resonance (J)

Λ eigenvalue of **K**-matrix

σ photoionization cross section (m^2)

τ lifetime of state (s)

A proportionality factor for cross section (m^2)

au   atomic unit

B   matrix in **QB** method

E energy (J)

E_i energy point in **K**-matrix method (J)

E_0 position of **K**-matrix pole on energy mesh (J)

E_r energy position of resonance (J)

g   parameter in **K**-matrix method (J)

h Planck's constant ($\simeq 6.6260693 \times 10^{-34}$ J.s)

$\hbar$ reduced Planck's constant ($= h/2\pi \simeq 1.0545717 \times 10^{-34}$ J.s)

i   imaginary unit ($\sqrt{-1}$)

I   identity matrix

k	Fano asymmetry factor
$\mathbf{K}$	reactance matrix in $\mathbf{R}$-matrix theory
K	single-element $\mathbf{K}$-matrix
K_i	scalar value of single-element $\mathbf{K}$-matrix at energy E_i
K_o	background contribution to $\mathbf{K}$-matrix
$\mathbf{M}$	lifetime matrix
M	single-element $\mathbf{M}$-matrix
M_{max}	maximum value of single-element $\mathbf{M}$-matrix
p	parameter in Fano profile
$\mathbf{Q}$	matrix in $\mathbf{QB}$ method
$\mathbf{R}$	resonance matrix in $\mathbf{R}$-matrix theory
$\mathbf{S}$	scattering matrix in $\mathbf{R}$-matrix theory
S	single-element $\mathbf{S}$-matrix

5 Appendix A: Using Lifetime Matrix to Investigate Single-Channel Resonances

In this Appendix we present the **K**-matrix method which is based on using the lifetime matrix **M** expressed in terms of the reactance matrix **K** to investigate single-channel resonances.

According to Smith [14], the **M**-matrix is given, in terms of the scattering matrix **S**, by

$$\mathbf{M} = -i\,\hbar\,\mathbf{S}^* \frac{d\mathbf{S}}{dE} \tag{11}$$

where $\mathbf{S}^*$ is the complex conjugate of **S**-matrix which is defined, in terms of **K**-matrix, by

$$\mathbf{S} = \frac{\mathbf{I} + i\mathbf{K}}{\mathbf{I} - i\mathbf{K}} \tag{12}$$

with **I** being the identity matrix, i is the imaginary unit, $\hbar$ is the reduced Planck's constant, and E is the energy. In the case of single-channel states, **M**, **S** and **K** are one-element matrices. To indicate this fact we annotate them with M, S and K. From Equations 11 and 12, the following relation can be derived

$$M = \frac{2}{1 + K^2} \frac{dK}{dE} \tag{13}$$

where $\hbar = 1$ in atomic units. It is noteworthy that since K is real, M is real as it should be.

Smith [14] has demonstrated that the expectation value of M is the lifetime of the state, τ. Now if K has a simple pole at energy E_0, given by

$$K = \frac{\text{g}}{E - E_0} \tag{14}$$

where g is a parameter with dimension of energy, then from 13 we obtain

$$
\begin{aligned}
M(E) &= \frac{-2\mathrm{g}}{(1+K^2)(E-E_0)^2} \\
&= \frac{-2\mathrm{g}}{(E-E_0)^2 + \mathrm{g}^2}
\end{aligned}
\tag{15}
$$

and hence the maximum value of $M(E)$ is $M(E_0) = -2/\mathrm{g}$. On substituting the half maximum, $-1/\mathrm{g}$, into Equation 15 we find

$$
E - E_0 = \pm\mathrm{g}
\tag{16}
$$

and therefore, the full width at half maximum is

$$
\Delta_E = |2\mathrm{g}|
\tag{17}
$$

According to Smith [14], the lifetime of the state τ, and the full width at half maximum, Δ_E, are related by

$$
\tau = \frac{1}{\Delta_E} \qquad \text{(au)}
\tag{18}
$$

Hence, for a **K**-matrix pole given by Equation 14 the autoionization probability, Γ^a, which by definition equals the reciprocal of the lifetime, is given in atomic units by

$$
\Gamma^a = \frac{1}{\tau} = \Delta_E = |2\mathrm{g}| \qquad \text{(au)}
\tag{19}
$$

Now if we consider a **K**-matrix with a pole superimposed on a background K_o

$$
K = K_o + \frac{\mathrm{g}}{E - E_0}
\tag{20}
$$

then from Equation 13 we find

$$
\begin{aligned}
M(E) &= \frac{-2\mathrm{g}}{(1+K^2)(E-E_0)^2} \\
&= \frac{-2\mathrm{g}}{(1+K_o^2)(E-E_0)^2 + 2K_o\mathrm{g}(E-E_0) + \mathrm{g}^2}
\end{aligned}
\tag{21}
$$

The maximum value of $M(E)$ occurs when the denominator has a minimum, that is when

$$
E = E_0 - \frac{K_o\mathrm{g}}{1+K_o^2}
\tag{22}
$$

and hence

$$
M_{max} = -\frac{2(1+K_o^2)}{\mathrm{g}}
\tag{23}
$$

This reveals that by including a non-vanishing background the peak of M is shifted relative to the pole position, $E = E_0$, and the peak value is modified. If we now calculate the full width at half maximum, Δ_E, by locating the energies where $M = \frac{1}{2}M_{max}$ from solving the quadratic

$$
(1+K_o^2)(E-E_0)^2 + 2K_o\mathrm{g}(E-E_0) - \frac{\mathrm{g}^2(1-K_o^2)}{(1+K_o^2)} = 0
\tag{24}
$$

we find

$$
\Delta_E = \frac{|2\mathrm{g}|}{1+K_o^2}
\tag{25}
$$

As full width at half maximum and autoionization probability are numerically equal in atomic units, we obtain

$$
\Gamma^a = \frac{|2\mathrm{g}|}{1+K_o^2} \qquad \text{(au)}
\tag{26}
$$

The two parameters of primary interest are the resonance position E_r and the resonance width Δ_r. However, for an energy point E_i with a **K**-matrix value K_i, Equation 20 has three unknowns, K_o, g and E_0 which are needed to find E_r

and Δ_r, and hence three energy points at the immediate neighborhood of E_0 are required to identify the unknowns. Since the **K**-matrix changes sign at the pole, the neighborhood of E_0 is located by testing the **K**-matrix value at each point of the energy mesh for sign change and hence the three points are obtained accordingly. Now, if we take the three consecutive values of K

$$K_i = K_o + \frac{\text{g}}{E_i - E_0} \qquad\qquad (i = 1, 2, 3) \tag{27}$$

and define

$$\Delta E_{jk} = E_j - E_k \qquad \& \qquad \Delta K_{jk} = K_j - K_k \tag{28}$$

then from Equation 27 we obtain

$$\Delta K_{12} = \text{g}\left(\frac{1}{\Delta \text{E}_{10}} - \frac{1}{\Delta \text{E}_{20}}\right) = \text{g}\left(\frac{\Delta \text{E}_{21}}{\Delta \text{E}_{10}\Delta \text{E}_{20}}\right) \tag{29}$$

$$\Delta K_{23} = \text{g}\left(\frac{1}{\Delta \text{E}_{20}} - \frac{1}{\Delta \text{E}_{30}}\right) = \text{g}\left(\frac{\Delta \text{E}_{32}}{\Delta \text{E}_{20}\Delta \text{E}_{30}}\right) \tag{30}$$

and

$$\frac{\Delta K_{12}}{\Delta K_{23}} = \frac{\Delta E_{30}\Delta E_{21}}{\Delta E_{10}\Delta E_{32}} \tag{31}$$

Therefore

$$\frac{\Delta E_{30}}{\Delta E_{10}} = \frac{E_3 - E_0}{E_1 - E_0} = \frac{\Delta K_{12}\Delta E_{32}}{\Delta K_{23}\Delta E_{21}} \tag{32}$$

On algebraically manipulating Equation 32 we find

$$\boxed{E_0 = \frac{E_1\Delta K_{12}\Delta E_{32} - E_3\Delta K_{23}\Delta E_{21}}{\Delta K_{12}\Delta E_{32} - \Delta K_{23}\Delta E_{21}}} \tag{33}$$

Having located the pole position, E_0, the following relation can be obtained from

Equation 29

$$g = \frac{\Delta K_{12} \Delta E_{10} \Delta E_{20}}{\Delta E_{21}} \tag{34}$$

Similarly, from Equation 27 we obtain

$$K_o = K_1 - \frac{g}{\Delta E_{10}} \tag{35}$$

Finally, E_r and Δ_r can be computed from Equation 22 and Equation 25 respectively.